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Thermodynamic and economic analysis of hydrogen production integration in the Brazilian sugar and alcohol industry



Jose Luz Silveira ^{a,b,c,*}, Celso Eduardo Tuna ^{a,b,c}, Wendell de Queiroz Lamas ^{a,b,c}, Marcio Evaristo da Silva ^{a,b,c}, Valdisley Jose Martinelli ^{a,b,c}

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ABSTRACT

One of the biggest challenges today is to develop clean fuels, which do not emit pollutant and with viable implementation. One of the options currently under study is the hydrogen production process. In this context, this work aims to study the technical and economical aspects of the incorporation process of hydrogen producing by ethanol steam reforming in the sugar cane industry and MCFC (molten carbonate fuel cell) application on it to generate electric power. Therefore, it has been proposed a modification in the traditional process of sugar cane industry, in order to incorporate hydrogen production, besides the traditional products (sugar, ethylic, hydrated and anhydric alcohol). For this purpose, a detailed theoretical study of the ethanol production process, describing the considerations to incorporate the hydrogen production will be performed. After that, there will be a thermodynamic study for analysing the innovation of this production chain, as well as a study of economic engineering to allocate the costs of products of the new process, optimising it and considering the thermoeconomics as being as an analysis tool. This proposal aims to improve Brazil's position in the ranking of international biofuels, corroborating the nation to be a power in the hydrogen era.

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*Corresponding author at: Sao Paulo State University, Department of Energy, Laboratory of Optimization of Energy Systems, Faculty of Engineering at Guaratingueta 333, Pedregulho, 12516–410 Guaratingueta, Brazil. Tel.: +55 12 3123 2836; fax: +55 12 3123 2835.

E-mail address: joseluz@feg.unesp.br (J.L. Silveira).

1. Introduction

Nowadays, economic and social reasons have spurred the use of ethanol as an alternative fuel and considered as one of the solutions for the environmental problems, such as increase of greenhouse effect, especially in the cities. Renewable fuels can be

^a Laboratory of Optimization of Energy Systems, Department of Energy, Faculty of Engineering at Guaratingueta, Sao Paulo State University, Guaratingueta 12516-410, Brazil

b Post-graduate Programme in Mechanical Engineering, Department of Mechanical Engineering, University of Taubate, Taubate, SP, Brazil

^c Department of Basic and Environmental Sciences, School of Engineering at Lorena, University of Sao Paulo, Lorena, SP, Brazil

obtained from biomass such as sugar cane, contributing to carbon sequestration. According to [1], ethanol is less toxic than methanol, a subject to be considered to spur its studies.

Silveira et al. [2] and Vasudeva et al. [3] have shown that the most recent application of hydrogen is in fuel cell, an available alternative for electricity generation, especially in far places.

The hydrogen storage is not practical. A high pressure is required because the poor energy density by volume. Safety issues are important. According to [2], fuel cells are interesting devices for decentralized generation of energy where the chemical energy found on the fuel is converted to electricity (direct current in low voltage) as seen in a work carried out by [4]. Table 1 shows the main fuel technologies.

Hydrogen is the simplest, the lightest, and the most plentiful element in the universe. It is made up of one proton and one electron revolving around the proton. In its normal gaseous state, hydrogen is colourless, odourless, tasteless, non-toxic, and burns invisibly (in the case of air mixture). It should not be considered a "fuel", but instead, it should be considered as an energy transport mechanism. Currently, more hydrogen is made from natural gas through a process known as reforming.

Nowadays, fuel cells are one of the most promising energy generation technologies. Many of these devices need hydrogen and oxygen for electricity production through electrolytic process, contrary to water electrolysis. According to [7], hydrogen is not available as primary source; it is necessary to get it in some fuels such as fossil hydrocarbons, biomass, or water, by electrolysis, for example.

Reformers are reactors that produce mixtures containing hydrogen, carbon dioxide, and some other compounds, throughout the process called steam reforming, where superheated water and hydrocarbons react to produce a mixture with hydrogen, carbon monoxide, and carbon dioxide. This process is endothermic. Hydrogen can also be produced from a variety of other sources including water and biomass [6].

Other process used for hydrogen production are partial oxidation (this reaction is exothermic) and auto thermal reforming. In partial oxidation, air, which contains gases such as oxygen and nitrogen, is used.

This work aims to study the process incorporation of hydrogen producing by ethanol steam reforming in the sugar cane industry, according to Fig. 1. In this case, in addition to the production of sugar and ethanol, the Brazilian sugar cane industry would be able to produce biohydrogen, to be used, i.e., with fuel cells, or for sale.

Table 1Main fuel cell technologies [5].

Fuel cell technologies	Electrolytes	Operation temperature ranges (°C)
AFC (alkaline) PEMFC (proton exchange membrane)	KOH Polymer membrane	50–200 50–90
PAFC (phosphoric acid) MCFC (molten carbonate) SOFC (solid oxide)	H ₃ PO ₄ K ₂ CO ₃ /Li ₂ CO ₃ ZrO ₂ /Y ₂ O ₃	180–210 600–750 800–1200

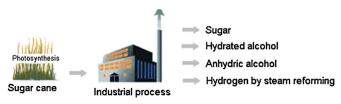


Fig. 1. New schematic of sugar cane industry [6].

2. Molten carbonate fuel cell

Selman [8] shows that molten carbonate fuel cells (MCFCs) are "the second generation" fuel cells. The first MCFC was developed by Broers and Ketelaar in the 1950s. This study is important because MCFC has high efficiency of generation using several fuels, contributing to low emission of pollutants.

According to [8], the MCFC has some issues:

The temperature of operation attains a range between 600 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$:

- It is generally used in nickel-based porous anode with chromium or aluminium and nickel oxide-based porous cathode doped with lithium.
- It is an alkaline carbonate electrolyte with LiAlO₂.

2.1. The electrochemical process

Silveira et al. [2] show that the reaction described in Eq. (1) occurs in the cathode. In this case, oxygen (O_2) reacts with carbon dioxide and electrons to produce carbonate ions (CO_3^2) , according to [9].

$$1/2O_2 + CO_2 + 2e \to CO_3^2 \tag{1}$$

The carbonate ions cross over the electrolyte, from cathode to anode. On the anode, the reaction described in Eq. (2) occurs. The oxidation of hydrogen uses the carbonate ions to produce steam and carbon dioxide, according to [9].

$$H_2 + CO_3^2 \rightarrow H_2O + CO_2 + 2e^-$$
 (2)

The electrochemical reaction is the oxidation of hydrogen, where transference of two electrons from anode to cathode occurs. Carbon dioxide can be transferred to cathode, where it is consumed.

On the anode, other fuel gases, such as carbon monoxide and methane, are used to produce hydrogen. Although the direct oxidation of carbon monoxide is possible, this act occurs at low velocity when compared with oxidation of hydrogen. However, the oxidation of carbon monoxide occurs, mainly through the reaction described in Eq. (3), called water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

The direct electrochemical reaction from organic fuels, such as methane, methanol, ethane, ethanol etc, is very slow. Because of this, steam reforming, which can be carried out in separated reformer (external reforming) or inside the fuel cell (internal reforming), is suggested.

2.2. Internal reforming process

Silveira et al. [2] show that internal reforming process occurs in fuel cells, which operate at high temperature, near electrochemically active devices. Fig. 2 shows some configurations about internal reforming process.

3. Thermodynamic analysis of ethanol steam reforming

Several technologies for hydrogen production may be studied. Steam reforming is one of the most usual technologies installed in chemical industries. The reforming efficiency is obtained through studying of physical-chemical properties of the components, thermodynamic conditions (temperature and pressure of reaction,

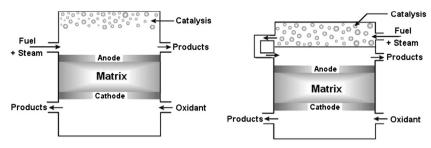


Fig. 2. Some internal steam reforming process configurations [2].

technical configurations of reformer such as dimensions and catalysts, and flows of materials). The method to be used depends on the suggested fuel cell.

Both external and internal reforming need catalysts. Internal reforming is only possible in fuel cells that operate at high temperature, e.g., MCFC and SOFC.

In the alumina support the metals activity order is Rh, Pd, and Pt. However, for ceria and zirconium supports the catalytic activity order is Pt, Rh, and Pd.

The fuel cell technology determines hydrogen purity and other reforming product rates. Steam reforming occurs in the presence of a catalyst, and the syngas produced includes hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), among others. Some arrangements to minimize some reactions that can contribute to decrease the hydrogen production are necessary. Since this reaction is endothermic, heat from external sources is necessary. To minimize losses, some products of steam reforming, such as non-reacted fraction of reactants, might be used to heat reactants, burning them through after-burners [6].

One of the most important is steam reforming of methane. One alternative is steam reforming of alcohols, especially ethanol. The use of this fuel is interesting in the Brazilian case, whereas Brazil is the greatest productor of this fuel in the world and it is the best way to guarantee the volume of production necessary. The integration or association of hydrogen production with sugar and alcohol industry, certainly, can put Brazil in a good classification in the 'hydrogen era', in the near future.

In the global reaction of hydrogen production using ethanol, six moles of hydrogen from one mole of ethanol are produced.

1. *Global reaction*. At high temperatures, reaction of ethanol and water in gaseous state results in the production of carbon dioxide and hydrogen, as shown by Eq. (4) [7];

$$C_2H_5OH_{(y)} + 3H_2O_{(y)} \rightarrow 2CO_{2(g)} + 6H_{2(g)}$$
 (4)

Ioannides [1] shows that the described overall reaction in Eq. (4) is done in the several stages.

2. Steam reforming reaction. Eq. (5) shows the steam reforming reaction, which is an endothermic reaction of ethanol with water, resulting in the production of carbon monoxide and hydrogen. This reaction may occur through an external reforming or inside a MCFC (internal reforming);

$$C_2H_5OH_{(\nu)} + H_2O_{(\nu)} \rightarrow 2CO_{(g)} + 4H_{2(g)}$$
 (5)

 Water gas shift reaction. It is an exothermic reversible reaction, as shown in Eq. (6), which can occur at lower temperatures than the latter reaction. However, the CO conversion is incomplete and an additional process to remove it is necessary;

$$CO_{(g)} + H_2O_{(v)} \to CO_{2(g)} + H_{2(g)}$$
 (6)

4. *Methanation*. Several chemical reactions can occur simultaneously with the steam reforming of ethanol reaction. Eq. (7)

shows a representative equation, which is the production of methane from carbon monoxide;

$$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$$
 (7)

5. *Bouduard reaction*. This reaction describes carbon formation by the decomposition of carbon monoxide as shown in Eq. (8).

$$2CO_{(g)} \to CO_{2(g)} + C_{(s)}$$
 (8)

The solid carbon formation during steam reforming process should be avoided so as not to decrease the conversion efficiency of the catalyst. To avoid this effect must be taken:

- Selecting the type of catalyst (metallic phase and support) to avoid any dehydration reactions;
- Controlling the ratio H₂O/EtOH—The carbon formation is disadvantaged with increasing ratio H₂O/EtOH;
- Optimal temperature control for type of catalyst selected.

The equilibrium constants associated with reactions previously studied may be expressed as Eqs. (9)–(12).

$$K_1 = \frac{y_{CO_2}^2 y_{H_2}^6}{y_{EIOH} y_{H_2O}^3} p^4 \tag{9}$$

$$K_2 = \frac{y_{CO}^2 y_{H_2}^4}{y_{EtOH} y_{H_2O}} p^4 \tag{10}$$

$$K_3 = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} \tag{11}$$

$$K_4 = \frac{y_{CH_4} y_{H_20}}{y_{CO} y_{H_2}^3} p^{-2} \tag{12}$$

where p is the pressure and y_i is a molar fraction of gaseous species, expressed in Pa, as Eq. (13).

$$y_i = \frac{n_i}{n_{tot}} \tag{13}$$

where n_i is the number of moles of each species, and n_{tot} is the sum of moles of all reactants or all products of reforming.

The equilibrium constants of reactions are linked with free energies of molecules in equilibrium. These energies can be implemented when an absolute temperature is fixed. After this, equilibrium constants can be calculated, as shown in [10].

A mathematical model is determined with the objective of calculating the latter Eqs. (9)–(13). Maggio et al. [10] show that when the fuel cell is producing electricity, voltage drop occurs in cathode (μ_c), anode (μ_a), and electrolyte. The resistance of fuel cell stuff also causes voltage drop. The electric potential difference of cell (U) is determined by Eq. (14).

$$U = U_0 - (\mu_a + \mu_c) - IR_i \tag{14}$$

where I is current density (A/cm²), R_i is internal resistance of cell (Ω cm²), and U_0 is equilibrium voltage (V), as shown in Nernst equation by Eq. (15) [8]. The electric potential difference of cell, the voltage drop, and equilibrium voltage are measured in volts (V).

$$U_0 = E_0 + \frac{R_G T}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2} p_{CO_2,c}}{p_{H_2O} p_{CO_2,a}} \right)$$
 (15)

where E_0 is standard voltage (V), R_G is universal constant of gases (8314 J/mol K), T is temperature of cell (K), F is Faraday constant (96,487 C/mole), and p_i is partial pressure of gases. The overall energy density is calculated through the sum of electric, thermal, and chemical energies, as shown in Eq. (16) [10].

$$W_{tot} = W_{el} + W_{th} + W_{ch} (16)$$

Densities of thermal and electric energies can be calculated as Eqs. (17) and (18), respectively.

$$W_{el} = VI \tag{17}$$

$$W_{th} = W_{cel} + W_{lat} + \frac{1}{5}C_1 \sum_{i} J_i (-\Delta H_i)$$
 (18)

where W_{cel} is the energy density due to electrochemically dissipated heat and Ohmic resistance (W/cm²), W_{lat} is the energy density due to latent heat of steam and ethanol (W/cm²), S is the cell surface (cm²), ΔH_i is the enthalpy (cal/mol) associated with reactions in steam reforming, which are (1) and (2), J_i is the output flow of gaseous species (mol/h), and C_1 is the conversion factor from cal/h to W (1163 × 10⁻³). The chemical energy density can be calculated through the gas volume that does not react, which may be burned as Eq. (19) [10].

$$W_{ch} = (-n_{EtOH}\Delta H_{EtOH} - n_{CH_4}\Delta H_{CH_4} - n_{CO}\Delta H_{CO} - n_{H_2}\Delta H_{H_2})S^{-1}$$
(19)

The thermodynamics of ethanol steam reforming for MCFCs has been studied by several researchers [11,12].

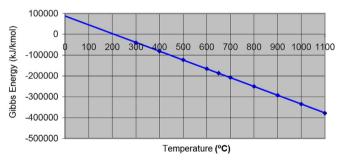


Fig. 3. Gibbs energy as function of temperature [13].

Table 2 Chemical equilibrium of global reaction of steam reforming of ethanol.

4. Physical-chemical analysis

4.1. Temperature influence

The dependence of Gibbs energy with temperature may be expressed by several parameters, following Eqs. (20) and (21).

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{20}$$

$$d\left(\frac{\Delta G^0}{T}\right) = -\frac{\Delta H^0}{T^2} \tag{21}$$

A steam reforming is an endothermic reaction, ΔH^0 is positive as equilibrium constant increases when temperature also increases. Fig. 3 shows Gibbs energy changes as function of temperature. At 480 K (207 °C), ΔG^0 is null, showing that the global reaction is possible only at high temperatures. According to the Le Chatelier principle, higher volume of products is formed at higher temperatures.

4.2. Equilibrium composition

The equilibrium composition as function of temperature can be determined, as shown in Table 2.

Assuming ideal conditions and excluding the fugacity coefficient, the equilibrium coefficient is equal to K_P (equilibrium constant as function of partial pressure of each component). The molar fractions of each species is determined by knowing the equilibrium coefficients (see Eq. (9)) and advance degree (α) of reforming, as shown in Eqs. (22) and (23), respectively.

$$K = \frac{3^3 \alpha^8 P^4}{(1+\alpha)^4 (1-\alpha)^4} = \frac{27\alpha^8}{(1-\alpha^2)^4} P^4$$
 (22)

$$\alpha = \frac{\sqrt[8]{K}}{\sqrt{\sqrt[4]{K} \pm \sqrt[4]{27P}}} \tag{23}$$

The equilibrium constant values, advance degrees, and molar fractions of hydrogen and ethanol as function of temperature in the range from 0 K to 1200 K and at 1 atm are calculated through Eqs. (22) and (23).

Graphics 4 to 7 were plotted based on chemical thermodynamic analysis, based on the Eqs. (22) and (23), and Table 2, subsequently the analysis, they were verified experimentally on a prototype of ethanol steam reforming developed at the Laboratory of Energy Systems Optimisation (LOSE) at Sao Paulo State University, Faculty of Engineering at Guaratingueta, Brazil.

The variation of advance degree as function of temperature can be seen in Fig. 4.

The yield of produced hydrogen and carbon dioxide and the yield produced hydrogen and non reacted ethanol as functions of temperature can be analysed, respectively in Figs. 5 and 6. In the two figures, the production of hydrogen achieves a maximum volume with temperatures near 600 K.

$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$								
Input								
Number of moles n_i Overall number of moles $n_{tot}^{(in)}$	п	$3n n_{\text{tot}}^{(\text{in})} = n + 3n = 4n$	0	0				
In equilibrium								
Number of moles n_i Overall number of moles $n_{rot}^{(eq)}$	$n(1-\alpha)$	$3n(1-\alpha)$ $n_{\text{tot}}^{(\text{eq})} = 4n(1+\alpha)$	$2n\alpha$	$6n\alpha$				
Molar fraction y_i	$\frac{1}{4}(1-\alpha)/(1+\alpha)$	$\frac{1}{3}\sqrt{(1-\alpha)}/(1+\alpha)$	$\frac{1}{2}\alpha/(1+\alpha)$	$3\frac{1}{2}\alpha/(1+\alpha)$				

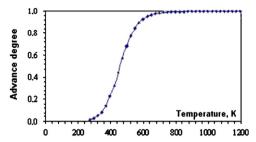


Fig. 4. Advance degree of global reaction of ethanol steam reforming as function of temperature The increase of temperature contributes to global reaction progress and, hence, the hydrogen production.

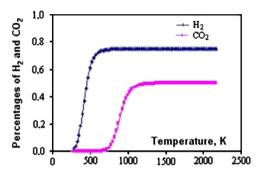


Fig. 5. Yield of produced hydrogen and carbon dioxide as function of temperature.

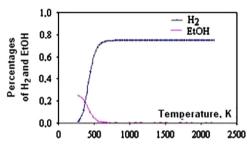


Fig. 6. Yield of produced hydrogen and non reacted ethanol as function of temperature.

4.3. Pressure influence

An increase of pressure of reforming contributes to decrease the advance degree and, consequently, decreases the hydrogen production.

Fig. 7 shows the behaviour of advance degree of global reaction of steam reforming of ethanol as function of pressure and temperature. With the exception of 300 °C, the advance degree does not present a great variation due to pressure variation.

According to Le Chatelier principle, an increase on operational pressure for the global reaction of ethanol steam reforming will provide a displacement on reaction balance in order to decrease the moles number. In other words, a pressure increase displaces the balance towards the reactants. The analyses of equations listed on Table 2 shows that pressure increase entails a decrease in advance degree of global reaction of ethanol steam reforming and consequently the hydrogen production decreases.

5. Economic analysis

The methodology of economic analysis is based on the method developed by [14], considering the feasibility of the sugar cane industry to produce 1500 N m³/h of hydrogen using ethanol. In order to reach this proposal, an economic analysis based on

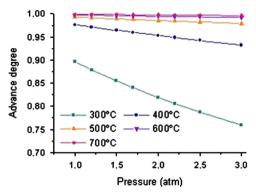


Fig. 7. Advance degree as function of pressure in five temperatures.

the investment of the hydrogen production system was developed, where were considered the input costs, operating cost, maintenance cost, operation period, interest rate and annuity factor.

According to [13] and [15], the following equations were used, Eqs. (9)–(13), in order to determinate the costs of hydrogen production.

The global equation for hydrogen cost is shown in Eq. (24).

$$C_{H_2} = \frac{Inv_{ref} \times f}{H \times \dot{E}_{H_2}} + C_{OP} + C_{MAN}$$
(24)

where $C_{\rm H2}$ is hydrogen production cost (US\$/kW h); $C_{\rm MAN}$ is maintenance cost (US\$/kWh); $C_{\rm OP}$ is operational cost (US\$/kW h); $E_{\rm H2}$ is energy provided by hydrogen (kW); f is annuity factor (1/year); H is equivalent period of operation (h/year); Inv_{ref} is reference investment for hydrogen production (\times 10⁴ US\$).

Operational cost using sugar cane bagasse as fuel is shown in Eq. (25) and according to [16], the maintenance cost of steam reformer was estimated as 3% of investment, Eq. (26).

$$C_{OP} = \frac{\dot{E}_{fuel} \times C_{fuel}}{\dot{E}_{H_2}} + \frac{\dot{E}_{EtOH} \times C_{EtOH}}{\dot{E}_{H_2}}$$
(25)

$$C_{MAN} = 0.03 \times \frac{Inv_{ref} \times f}{H \times \dot{E}_{H_2}}$$
 (26)

where E_{fuel} is energy provided by sugar cane bagasse (kW); C_{fuel} is fuel cost (sugar cane bagasse) (US\$/kW h); C_{EtOH} is ethanol cost [US\$/kW h]; E_{EtOH} is energy provided by ethanol (kW).

The equation of annuity factor (f) is shown in Eq. (27) and the equation of capital value (q) is shown in Eq. (28).

$$f = \frac{q^k \times (q-1)}{q^k - 1} \tag{27}$$

$$q = 1 + \frac{r}{100} \tag{28}$$

where k is payback period (year); r is annual interest rate (%).

The reference investment (Inv_{ref}) was estimated using Boehm's technique [17], and its application is based on Fig. 8.

$$C = C_r \left(\frac{S}{S_r}\right)^m \tag{29}$$

Silva [14] has adapted the reference investment for steam reform process with hydrogen production range from $1 \text{ N m}^3/\text{h}$ to $1500 \text{ N m}^3/\text{h}$, resulting in Eq. (30).

$$Inv_{ref} = 400 \left(\frac{m_{H_2}}{750}\right)^{0.5304} \tag{30}$$

6. Results and discussion

In thermodynamic studies of steam reforming of ethanol at the temperature range of MCFC, three temperatures were chosen (600 °C, 650 °C, and 700 °C) at 1 atm for the proposed system. A mathematical model is used to calculate the equation system, where system balance was used, considering all input and output flows, the stoichiometric reaction, and operational conditions (temperature and pressure). The influence of temperature in the voltage of cell can be analysed in Fig. 9, which presents voltage as function of current density of cell, as shown by [11].

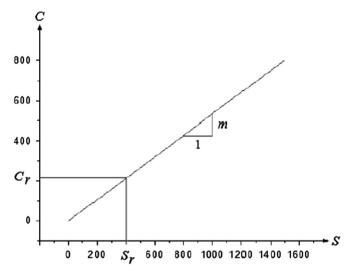


Fig. 8. Auxiliary curve to determine the reference cost through Fig. 8 was able to obtain Eq. (29).

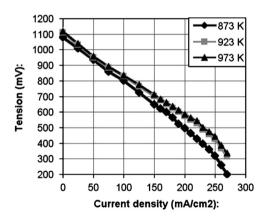


Fig. 9. Voltage as function of current density [9].

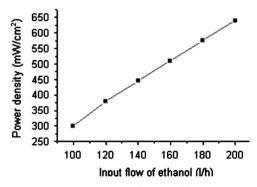


Fig. 10. Power density as function of fuel input.

The voltages in open circuit decrease when operation temperatures also decrease (1.12 V at 973 K; 1.10 V at 923 K; 1.08 V at 873 K). This fact occurs due to the reduction of hydrogen volume available in the anode, reactant produced by steam reforming process, which is dependent on cell temperature. The gaseous flow from reforming contains a percentage of hydrogen that varies from 46.8% to 58.9% when the temperature varies from 873 K to

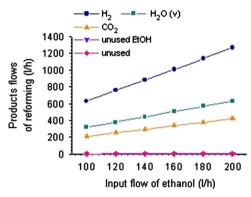


Fig. 11. Input flow of fuel (L/h) and product flow of reforming (L/h).

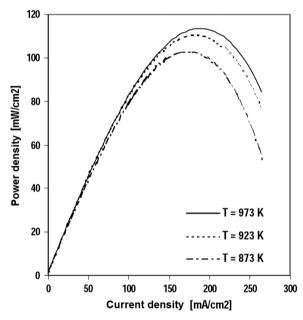


Fig. 12. Power density as function of current density of cell [2].

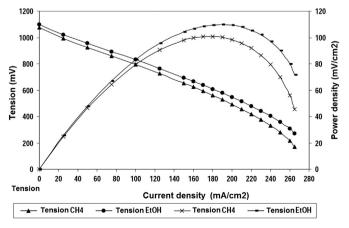


Fig. 13. Comparison with methane and ethanol as fuels for DIR-MCFC [2].

973 K, as shown by [2]. The current density calculated is about 280 mA/cm^2 , independent of temperature and pressure. It is also important to see the power density of fuel. Fig. 10 shows the density of power as function of input flow of ethanol in the following conditions: T=923 K; P=1 atm; $R_i=0.75 \text{ W cm}^2$, as shown by [18].

The power density increases when input flow of fuel also increases. This fact is due to the increasing production of hydrogen. The increase of power density can be seen when reforming product flow is associated with ethanol input flow, as shown in Fig. 11.

Fig. 12 shows the power density as function of current density for three temperatures chosen (973 K, 923 K, and 873 K) at 1 atm.

The energy produced has a maximum point at 190 mA/cm² (99.8 mW/cm², 109.8 mW/cm², and 113.7 mW/cm² for 873 K, 923 K, and 973 K, respectively). However, the curves are limited in high current density due to lack of hydrogen, as shown by [2].

The performance of DIR-MCFC using ethanol of fuel can be compared to the same cell using methane as fuel, as shown in

Hydrogen production cost as function of the payback period, H=4000 h/year

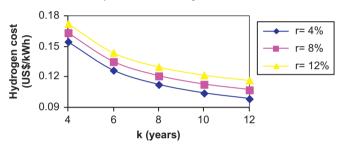


Fig. 14. Hydrogen production cost for anhydrous ethanol as function of payback period for different annual interest rate.

Hydrogen production cost as function of the payback period, H=4000 h/year

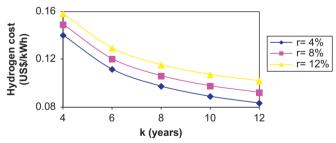


Fig. 15. Hydrogen production cost for hydrated ethanol as function of payback period for different annual interest rate.

Hydrogen production cost as function of the annual interest rate, H=4000 h/year

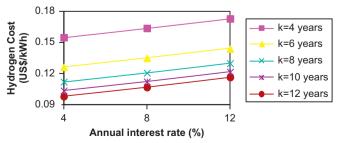


Fig. 16. Hydrogen production cost as function of annual interest rate with different payback period for anhydrous ethanol.

Hydrogen production cost as function of the annual interest rate, H= 4000 h/year

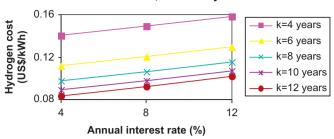


Fig. 17. Hydrogen production cost as function of annual interest rate with different payback period for hydrated ethanol.

Hydrogen production cost as function of the annual interest rate, k = 8 years

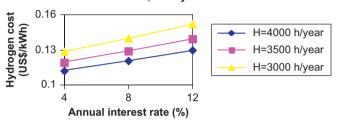


Fig. 18. Hydrogen production cost as function of annual interest rate for anhydrous ethanol with different utilization period.

Hydrogen production cost as function of the annual interest rate, K= 8 years

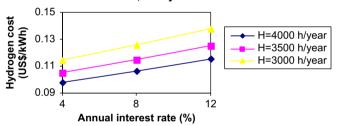


Fig. 19. Hydrogen production cost as function of annual interest rate for hydrated ethanol with different utilization period.

Comparison between Hydrogen production cost for different kind of ethanol, annual interest rate=12%. H=4000 h/year

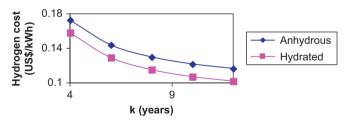


Fig. 20. Comparison between hydrogen production cost for different kind of ethanol as function of payback period.

Fig. 13. The conditions of operation considered are 923 K, 1 atm, and steam/fuel ratio equal to 2, as shown by [2]. Input flows of methane and ethanol equal to 142.5 L/h and 95 L/h, respectively, are considered.

For calculations were used the value of 0.7961 L/h obtained by [14] as experimental result of anhydrous ethanol amount for producing 1 N $\rm m^3/h$. Based on this previous study, it was obtained the value 0.8597 L/h for hydrated ethanol.

With these two parameters and adopting the hydrated ethanol cost is 70% of anhydrous ethanol, it was possible to make a comparison between them. Figs. 14-20 present an equivalent period of operation (H) of 4000 h/year.

Fig. 14 presents the hydrogen production cost as function of payback period for anhydrous ethanol. The annual interest rate (r) ranged from 4% to 12%. As expected, the results show that the production cost decreases with the increase of payback period (k). Higher interest rates increase the cost of production.

Fig. 15 presents the hydrogen production cost as function as payback period for hydrated ethanol. The result shows the same behaviour obtained for anhydrous ethanol.

Fig. 16 shows the hydrogen production cost as function of annual interest rate, with different payback period for anhydrous ethanol. This result is in accordance with previous results. The same behaviour is presented in Fig. 17 for hydrated ethanol.

Fig. 18 shows the hydrogen production cost as function of annual interest rate with different equivalent period operation, for payback period of 8 years. The same features are shown for hydrated ethanol, as can be seen in Fig. 19.

Fig. 20 shows the comparison between hydrogen production cost for anhydrous and hydrated ethanol as function of payback period. It is noticeable that hydrated ethanol presents hydrogen production cost lesser than anhydrous ethanol because the hydrated ethanol price was considered 70% of anhydrous ethanol price.

7. Conclusions

This work was developed to show the advantages of hydrogen producing from ethanol steam reforming and to show what kind of ethanol would be more viable to hydrogen production: the anhydrous or hydrated. Although the anhydrous ethanol has higher lower heating value and demanded less ethanol amount to produce 1 N m³/h of hydrogen, the results of economic analysis showed that hydrated ethanol is more viable than anhydrous ethanol. The main reason for this behaviour was the cost difference between anhydrous and hydrated ethanol, in the specific situation of this work, the hydrated ethanol cost was adopted as being 70% of anhydrous value. The results showed that hydrated ethanol is the best alternative to produce hydrogen in the production chain of sugar cane industry.

The theoretical results obtained in this work show relations with operational conditions and energetic factors that are important parameters for study of availability of steam reforming of ethanol in a DIR-MCFC.

Through studies done, it was concluded that with increase of reforming temperature, the increase of voltage and current density occurred due to higher production of hydrogen.

It is feasible to work with a fuel cell in current density near 190 mA/cm², where the greatest energy densities are registered. This fuel cell model is a good alternative for cogeneration systems because the use of products from steam reforming at high temperatures is possible.

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